Progress on the Synthesis of a Symmetrical Dihydroxydibenzo-26-crown-8

An Honors Thesis (HONRS 499)

By

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Abstract

Crown ethers complex selected metal ions, ammonium ions, and potentially, other electron deficient species. With proper functionalization a crown ether might sequester and signal the presence of ions or electron deficient molecules; or from the other perspective, complexed ions or molecules might alter the conformation and properties of the crown ether. The target dihydroxydibenzo-26-crown-8 (1) is designed to be an attachable jaw that can be combined with one or two chromophores to produce fluorescent chemosensors. Progress towards the preparation of this new 26-crown-8 will be presented. Known intermediates such as bis-1,2[2-hydroxyethoxy]benzene(2) and bis-1,2[2-(3-chloro-2-hydroxypopoxy)ethoxy]benzene(3), and a protected bis-1,2[2-(3-chloro-2-hydroxypopoxy)ethoxy]benzene(5) using Dihydropyran have been synthesized. Our approaches to the formation of the "jaw" crown ether (1) by reaction of (2) with (5) will be described.

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Introduction:

Crown Ethers

Crown ethers are heterocyclic chemical compounds that, in their simplest form, consist of repeating -CH_2CH_2O- units. These compounds were first discovered in 1967 as an unexpected byproduct of a synthesis reaction performed by Charles Pedersen[7]. While trying to prepare a complexing agent for divalent cations by linking two Catechol molecules through one hydroxyl group on each molecule, he was surprised to isolate a byproduct that bound or complexed with potassium cations but had no ionizable hydroxyl group. He pursued the research further by creating thirty-three of these "cyclic polyether" compounds to discover their unique ability to complex with metal cations and electron-deficient species due to the inwardly facing oxygen atoms that are ideally situated to coordinate with a cation in the interior of the ring. He named them "crowns" because when this special group of heterocycles binds to cations the complex resembles a crown sitting on a head. It was initially believed that the stoichiometry of the complexes was one molecule of polyether per single ion regardless of the valence; however, it has since been discovered that a few very large crowns can have two complexed cations at one time[9].

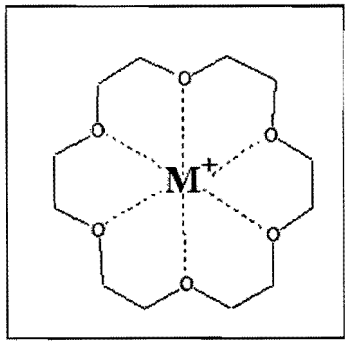


Figure 1: an 18-crown-6 compound showing non-covalent interactions and complexation of metal ion with inwardly facing oxygen atoms. Generally only one ion will complex with one crown compound at a given time.

Another important feature of the crown complexes involves their selective complexation ability. Because of this unique property, particular ions can be targeted while creating crown ethers based on the size of the cavity of the crown, diameter of the target cation, number of donor atoms in the crown, and charge number of the target cation[7]. This molecular recognition behavior has helped bridge one of the fundamental gaps between biological reaction and artificial chemical reaction. Since Pederson's discoveries many investigations on the analyses of these structures, their characteristics, as well as applications have been developed.

The United States Patent and Trademark Office currently lists twenty-nine patents involving crown ether compounds ranging from 1974-2006. The earliest patents used crown ethers as catalysts for the polymerization of conjugated dienes, lactam, and 2-pyrrolidone and caprolactam[10]. Through what is known as "host-guest" chemistry, scientists have been able to develop simple organic compounds that mimic enzymatic activity as phase transfer catalysts (PTC's). PTC's facilitate the migration of a particular chemical component from one phase into another phase in a heterogeneous system. For example, a specific chemical component could be soluble in one phase but insoluble in the other unless the phase transfer catalyst is present. In the case of crown ethers, even though the interior of the ring is highly hydrophilic, the exterior of the ring is hydrophobic. The result is that the complexed cation can become soluble in non-polar solvents[4].

More recent developments in crown ether technology have been focused on crown ethers as chemical sensors or "chemosensors." By attaching specialized functional

groups to the crown ether compounds, target cations bonded through non-covalent interactions will produce a change in light absorption or fluorescence, which can be monitored and measured. A key requirement of chemosensor function is that the cation binding occur reversibly (non-covalently). This allows cation concentration to be measured at equilibrium by optical detection of either the chemosensor-bound species or the cation-free chemosensor. It also allows for continuous measurements to be made with dynamic optical response to changing cation concentration[2].

A current U.S. Patent exists for a fluorescent ion-selective diaryldiaza crown ether that is primarily useful for detection and quantitation of alkali-metal ions in aqueous solution. Such indicators are useful for measuring ions in extracellular spaces; in vesicles; in vascular tissue of plants and animals; biological fluids such as blood and urine; in fermentation media; in environmental samples such as water, soil, waste water and seawater; and in chemical reactors[8].

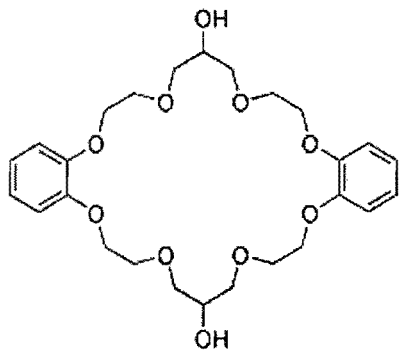
Another example of chemosensor technology was implemented at the NIEHS Marine and Freshwater Biomedical Sciences Center at the University of Miami where several crown ethers were attached to fluorescent molecules used to monitor the level of harmful marine toxin saxitoxin from red tides. For economic and ethical reasons, these fluorescent crown ether sensors were meant to replace prior methods including biological assays and expensive and time-consuming analytical equipment[5].

Abiotic chemosensors are being tailored for a vast amount of target molecules, and their physical properties engineered to meet specific sensor requirements. These are added advantages compared to biotic receptors that are sensitive to pH, oxidizing agents and heat, which may be necessary conditions for some analytical devices[2]. Currently,

extensive research is being carried out into the development of large supramolecular chemosensor compounds that are highly specific and have extensive signaling attachments and have oxygen donor atoms replaced with "softer" bases such as nitrogen, sulphur, and phosphorous[7].

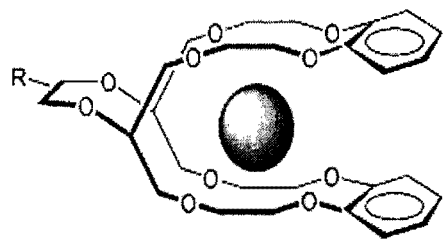
Rationale for Research

Our target molecule is a Dihydroxydibenzo-26-Crown-8(1). It is our belief that our molecule could be used as a chemical sensor for important ions, or electron deficient pi systems. Based on the design of the molecule, the crown would collapse like a jaw when complexed with a specific ion. Fluorescent molecules would be attached at the hydroxyl backbone of the crown and would emit fluorescence of some kind as a result of the bending induced after complexation with a specific ion. This fluorescence could be measured under ultraviolet light and measured in a UV-visible spectrometer. The conformational changes induced after complexation may also be observed with carbon-13 NMR. By being able to measure this interaction between our crown and its specific target ion, we will be able to measure ion concentrations in a non-invasive manner, which would be less time-consuming, more cost effective, and less detrimental to the solution being observed than with current methods. We have proposed a few methods of producing these results from our crown.



Single fluorescent molecule attachment

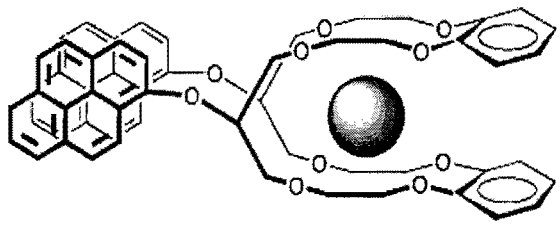
One fluorescent molecule would be attached to both hydroxyl groups of the crown. As the crown clamps in the presence of positive metal ions or organic compounds bearing a positive charge, the molecule attached at the hydroxyl groups would flex and emit altered fluorescence or absorb light at a different wavelength allowing the concentration of the electron deficient compound to be determined by fluorescence measurements or UV spectra analysis.



Induced Excited Dimer Formation

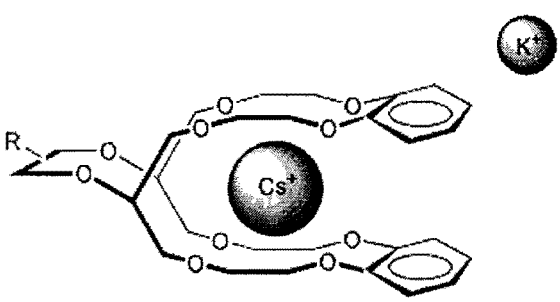
Separate fluorescent molecules would be attached at each hydroxyl group of the crown. When the crown collapses in presence of an electron deficient molecule or a cation, the fluorescent molecules would be drawn together, forming an excited dimer,

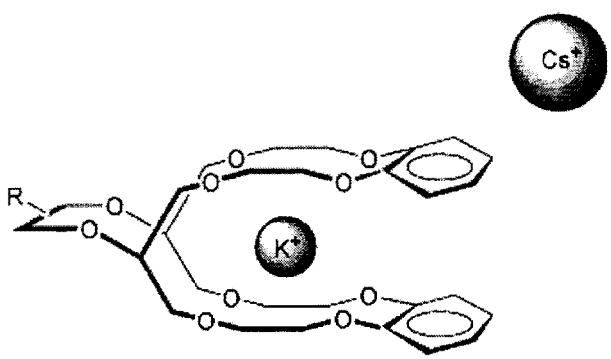
which may emit fluorescence that can be viewed in the visible spectrum or measured in Carbon-13 NMR.



Displacement of a Quencher

With one fluorescent molecule attached to both hydroxyl groups, large atoms such as Cesium would quench the fluorescence of the molecule. When smaller atoms such as Potassium displace these larger atoms, the crown would bend more and flex the molecule attached at the hydroxyl backbone, which could induce changes in fluorescence and the carbon-13 NMR. This would allow us to distinguish between ions in a solution consisting of multiple electron deficient particles.

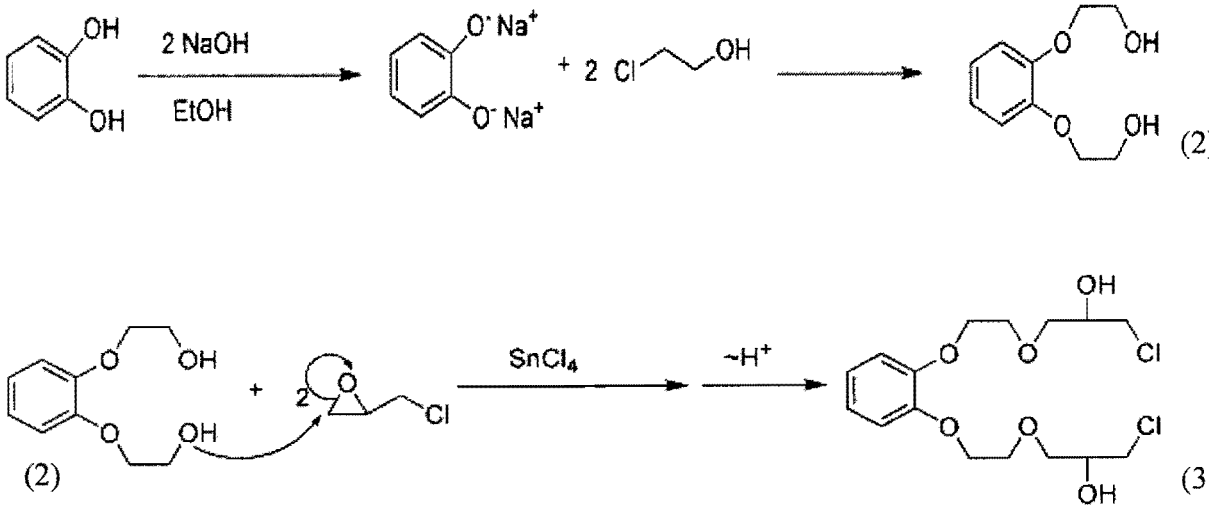


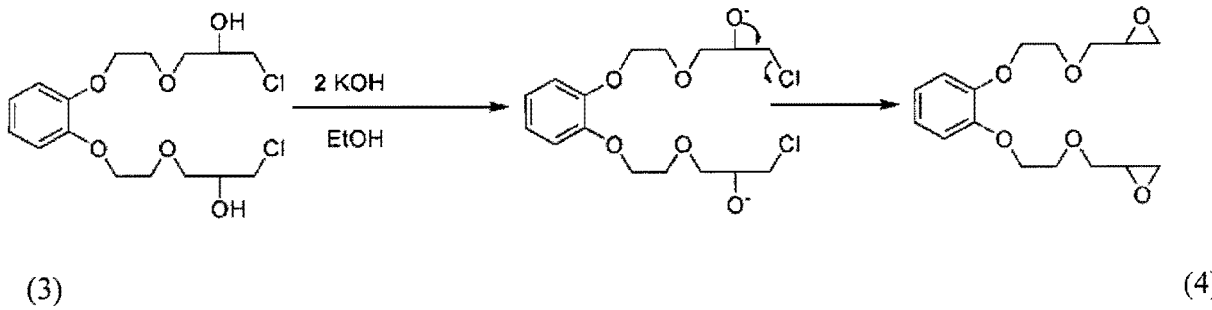


Synthetic Plans

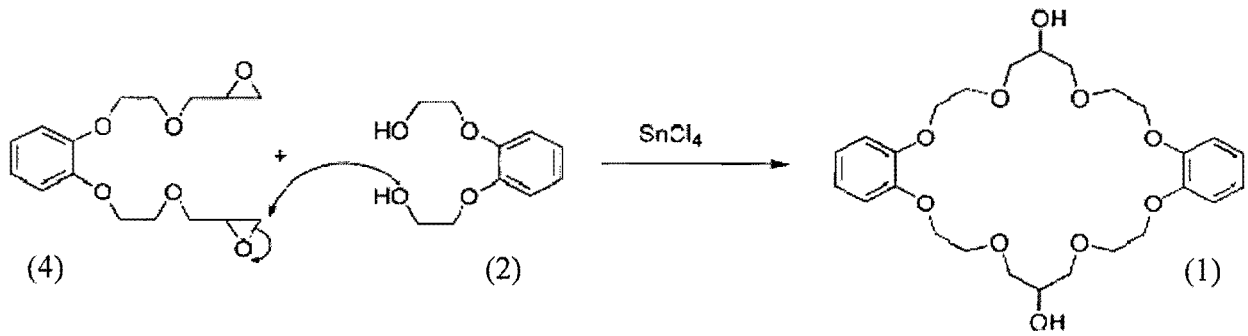
Our plan for the Dihydroxydibenzo-26-crown-8(1) synthesis was to take a multi-step approach starting from Catechol and progressively adding extensions to the 1,2 hydroxyl groups. From this method, we would build a large two-armed molecule that would be closed off to form a ring in a final step.

Scheme 1



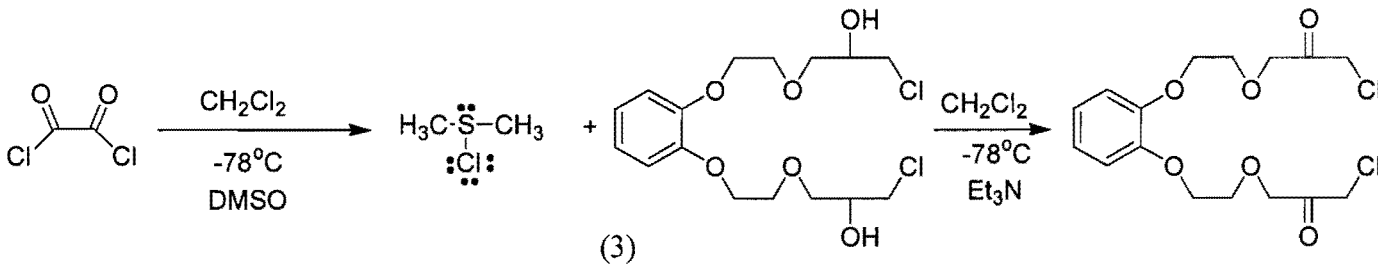


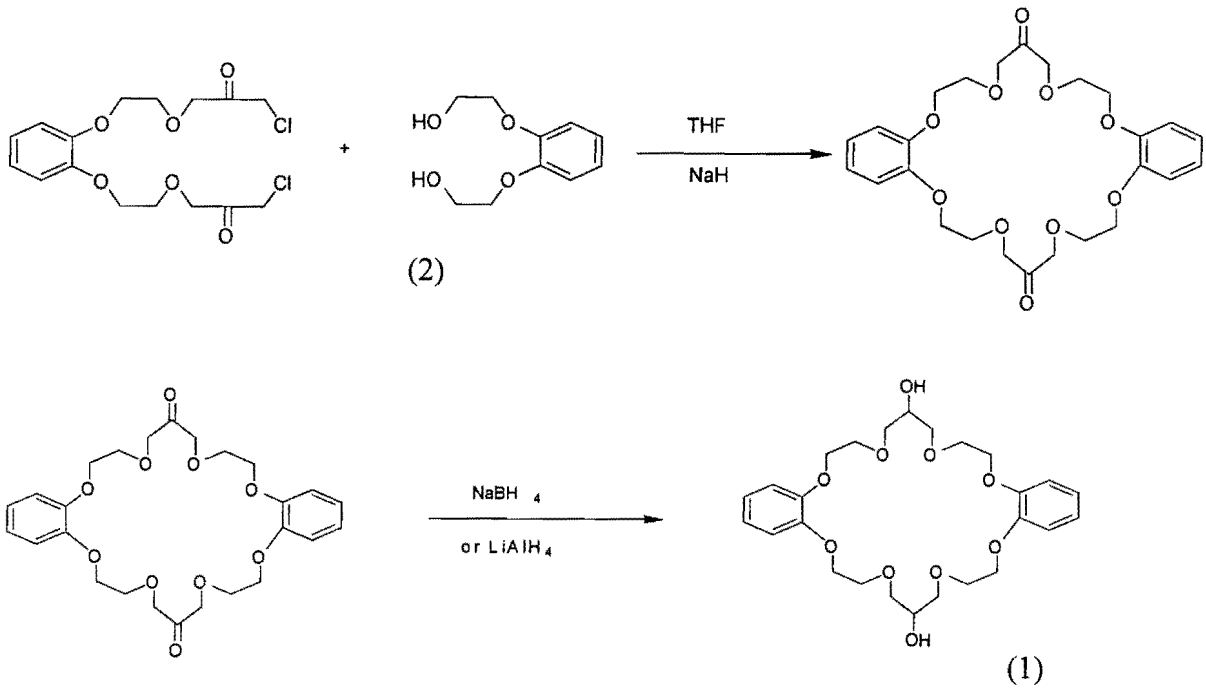
(3) (4)



In our initial attempt to develop the Dihydroxydibenzo-26-Crown-8(1), we reacted 1,2-bis[2-hydroxyethoxy]benzene(2) with Epichlorohydrin to create 1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene(3). We then reacted compound (3) with a strong base (KOH) to develop 1,2-bis[2-(2,3-epoxypropoxy)ethoxy]benzene(4). Similar to the reaction with Epichlorohydrin to form compound (3), we used Tin(IV) Chloride as a catalyst to react compound (2) with compound (4) in hopes of forming our target molecule, compound (1). To date, our research group has made a number of attempts with different sets of conditions. A recent approach has given preliminary indications of possible success[1].

Scheme 2 (The Swern Oxidation)[1]



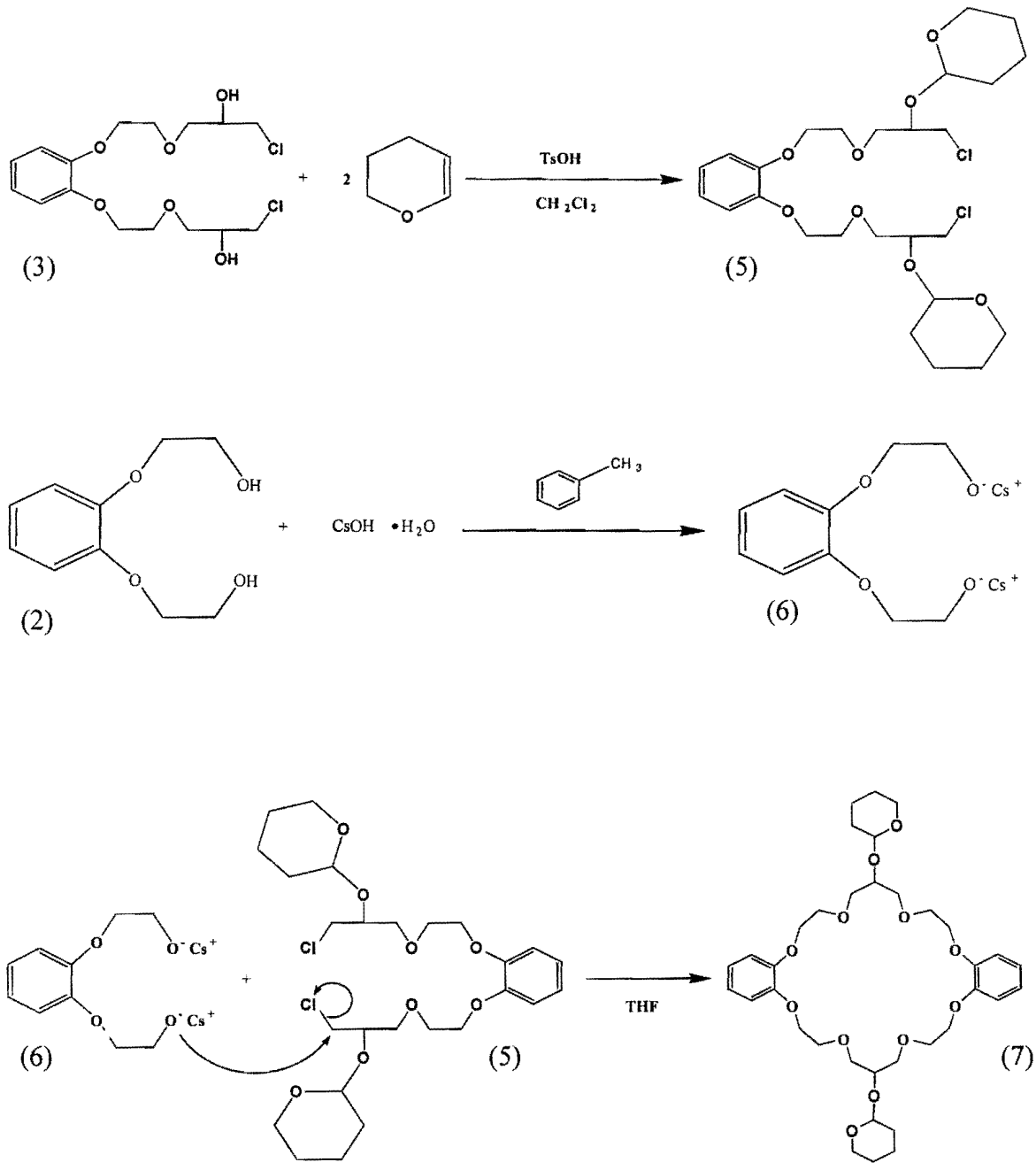


(2)

(1)

As a result of the 1,2-bis[2-(2,3-epoxypropoxy)ethoxy]benzene(4)'s stubbornness to react, we attempted to create a more reactive molecule in order to add the 1,2-bis[2-hydroxyehtoxy]benzene(2) to complete the crown synthesis. We decided to utilize a Swern oxidation on compound (3) to form a more reactive α-chlrorcarbonyl compound. Unfortunately, we discovered the α-chlrorcarbonyl compound was too reactive and formed polymers[1].

Scheme 3 (Protection with THP)



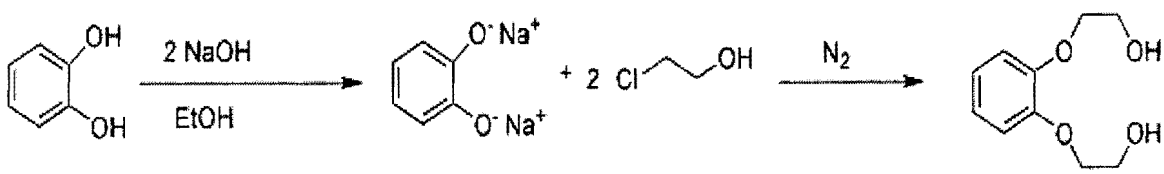
In our latest approach, we decided to try protecting the hydroxyl groups of the 1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene(3) using Dihydropyran to

prevent any temptation towards a polymerization reaction. As previously proposed, we would then react the protected compound with 1,2-bis[2-hydroxyethoxy]benzene(2) to create the dibenzodihydroxy-26-crown-8(1). The 1,2-bis[2-hydroxyethoxy]benzene(2) would first be reacted with CsOH to form a salt compound (6) that would potentially help form the crown by using the cesium ions to complex with the crown as a template to induce folding.

We decided to use Dihydropyran because many other alcohol protecting groups such as MOM and MEM compounds required the use of strong base to be attached, which could possibly reform the diepoxide compound we attempted in scheme 1[6]. Dihydropyran is attached using an acid (TsOH) catalyst[3], which is more compatible with our compound. Our only concern with using Dihydropyran was adding chiral centers to the compound, increasing the number of stereoisomers, and creating confusion in the NMR.

Results and Discussion:

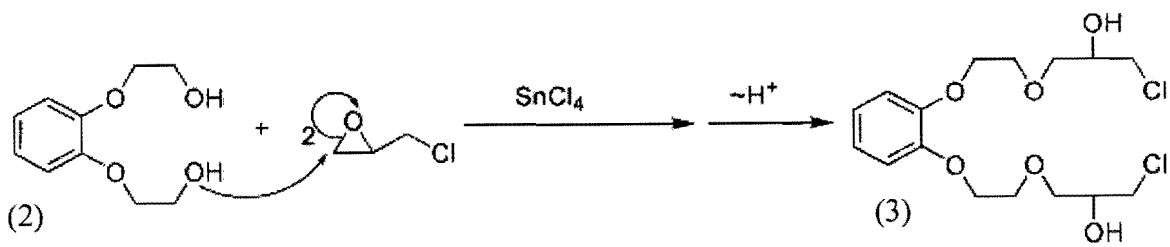
Synthesis of 1,2-bis[2-hydroxyethoxy]benzene(2)



(2)

In a typical reaction, (2) was recovered giving a 29.3% yield. Yields from this experiment ranged from 25-30% in most cases with a melting range from 77-83°C. Some possible reasons for our low yields include oxidation of the reagent catechol while changing the reaction apparatus. We also discovered that the 1,2-bis[2-hydroxyethoxy]benzene(2) product was slightly soluble in water and may have been lost during the workup. Some product was recovered from the waste material by re-dissolving it in Ethyl Acetate, but not enough could be extracted to significantly improve our final yield. Proton and Carbon-13 NMR were taken upon recrystallization of our product. (**See Appendix A**)

Synthesis of 1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene(3)

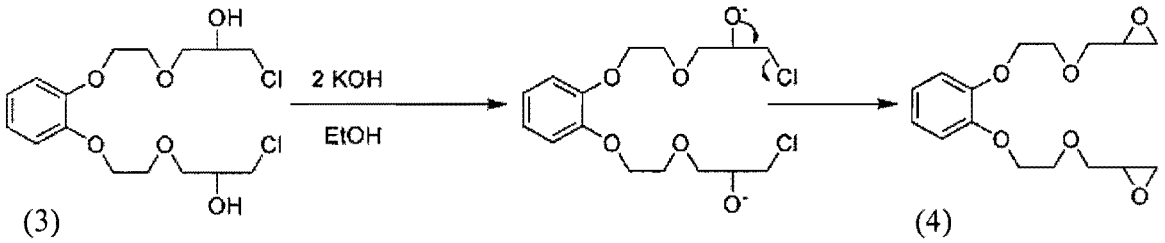


After all reagents were added to the round-bottom flask and allowed to reflux at 70°C, thin-layer chromatography (TLC) was taken every 30 minutes and developed in 5% Methanol in Dichloromethane until the 1,2-bis[2-hydroxyethoxy]benzene(2) had faded. The solution was then worked up according to the experimental protocol. The remaining product (3) was a golden syrupy compound that produced a crude yield of

approximately 83.5% in most cases. We found that it was crucial to stir the 1,2-bis[2-hydroxyethoxy]benzene(2) for at least 4 hours under argon gas to remove all traces of oxygen and water before reacting with Tin(IV) Chloride catalyst and Epichlorohydrin. Otherwise, yields dropped significantly. Proton and Carbon-13 NMR were taken of our product. **(See Appendix A)**

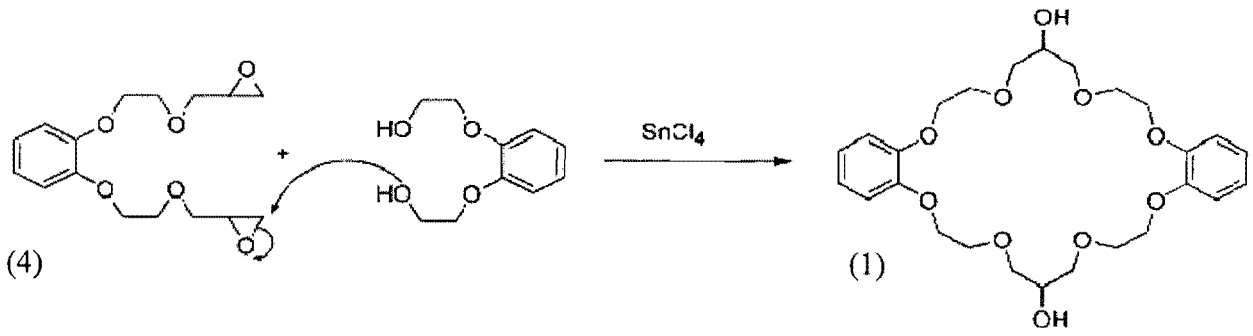
Scheme 1

Synthesis of 1,2-bis[2-(2,3-epoxypropoxy)ethoxy]benzene(4)[1]



To protect this reaction from absorbing water, a Calcium Chloride drying tube was placed on top of the round-bottom flask. TLC was taken every 15 minutes and developed in 5% Methanol in Dichloromethane until the 1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene(3) had faded. After the product was worked up, the remaining solvent was evaporated under high vacuum without heat. Heating the 1,2-bis[2-(2,3-epoxypropoxy)ethoxy]benzene(4) resulted in polymerization. In a typical reaction, 6.27g (19mmol) of crude product was recovered resulting in a 95% yield[1]. Proton and Carbon-13 NMR were taken of our product. **(See Amoozgar, 2006-2007)**

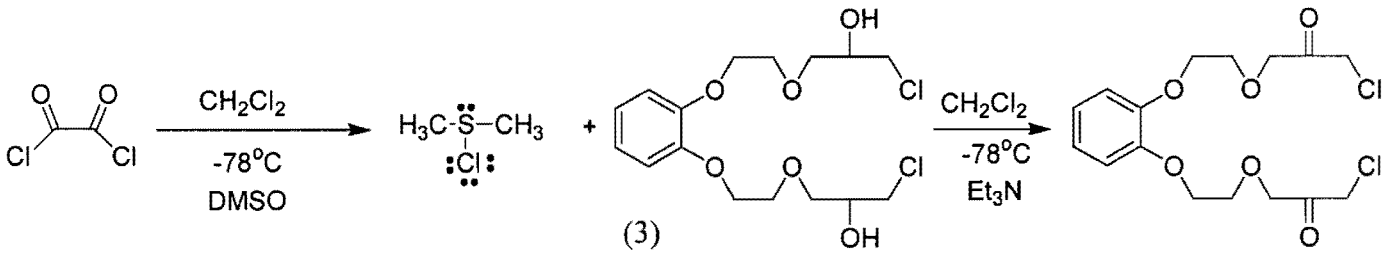
Synthesis of dihyroxydibnezo-26-crown-8(1)[1]



We observed 1,2-bis[2-(2,3-epoxypropoxy)ethoxy]benzene(4) to be much less reactive than expected. After several attempts we were unable to react (4) without polymerization. The synthesis of the dihyroxydibnezo-26-crown-8(1) was unsuccessful by this method[1]. New reaction conditions are being investigated by a research colleague.

Scheme 2

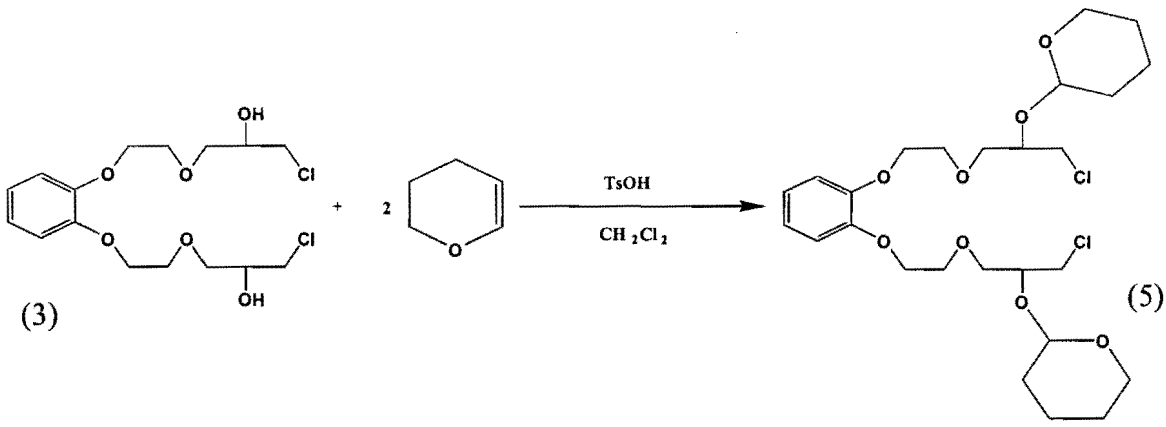
The Swern Oxidation[1]



The α-chlrorcarbonyl compound created from the Swern oxidation was found to be extremely reactive. We were unable to control our reaction and prevent polymerization. This method also failed to produce our target molecule, the dihyroxydibnezo-26-crown-8(1)[1].

Scheme 3

THP protection

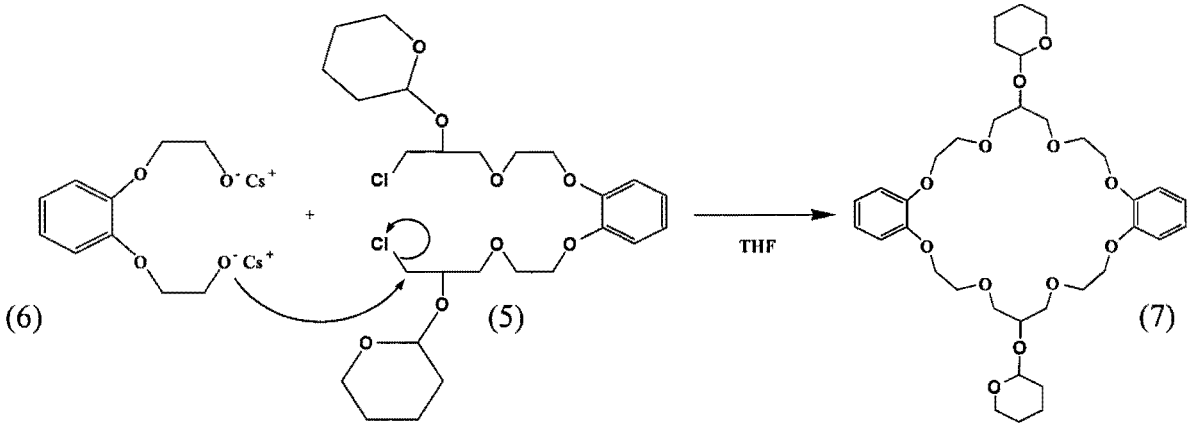


(3) (5)

This being our first attempt at this experiment, we were a bit uncertain about what to expect. We based our protocol primarily on our source from the *Journal of Organic Chemistry*[3]. We kept mole ratios and procedures the same from the original protocol described in the article. We were able to recover 6.221g of a syrupy crude product which produced a crude yield of 116%. From a proton and carbon-13 NMR prediction program available on ChemDraw, we were able to approximate our absorption peaks from our own NMR spectra of our crude product **(See Appendix A)**. By comparing our experimental data with the predicted results from the ChemDraw software, we were fairly confident the reaction was successful.

One possible explanation for this excessive yield would be the presence of extra solvent that may not have been completely removed during the rotary evaporation. Based on the results described in the article, we assumed a 95% yield for our calculations in the next step of the reaction. The crude product was placed on an oil pump overnight to remove any traces of excess solvent and/or water.

Synthesis of the Protected Dihydroxydibenzo-26-Crown-8(7)



(6) (5) (7)

Once again, we collected a yield of crude product above 100%. After the solvent was removed using rotary evaporation and vacuum pumping, 6.833g of slush remained. Proton and Carbon-13 NMR were taken and again compared with the predicted NMR produced from the ChemDraw software. We observed several multiplet peaks in the proton NMR, which were difficult to distinguish. We saw evidence that there was 1,2-bis[2-hydroxyethoxy]benzene(2) and the protected 1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene (5) in our solution, but no distinguishing peaks that would imply the presence of the dihydroxydibenzo-26-Crown-8(7). Based on the

predicted spectra from the ChemDraw software, there are many similarities between the spectra of compound (5) and compound (7). **(See Appendix A)**

Our plans for the future are to perform chromatography on the solution to remove as much of compound (2) along with any other side products that may be present. We will then re-analyze the solution using proton and Carbon-13 NMR to better confirm or deny the presence of the protected crown (7).

Experimental Section:

Reagents and Materials:

Sodium Hydroxide, Absolute Ethanol, Catechol (99+%), 2-Chloroethanol (99%), Ethyl Acetate (99.5%), Sodium Sulfate (Anhydrous), Tin(IV) Chloride (99.995%), Epichlorohydrin (99+%), Ethyl Ether, Chloroform-D (+0.05% V/V TMS), KOH, Dichloromethane (Low Water), 3,4-Dihydro-2H-pyran (97%), Sodium Bicarbonate, Toluene, *p*-Toluenesulfonic Acid Monohydrate (98.5+%), Cesium Hydroxide Monohydrate, (min 90%).

Synthesis of 1,2-bis[2-hydroxyethoxy]benzene (2)

Sodium Hydroxide (24.012g, 600mmol) was added to 300mL of Absolute Ethanol (abs. EtOH) in a 1000mL 3-neck round-bottom flask. The flask was slightly heated using a heating mantel with the variac setting at 15. Argon gas was passed over

the system for one hour to purge the system of oxygen. Catechol (27.447g, 250mmol) was then added to the system, forming a chunky, white precipitate in a dark green solution. 2-Chloroethanol (40mL, 600mmol) was dissolved in 50mL of Absolute Ethanol and added drop wise to the reaction mix. The solution was then stirred and allowed to reflux (variac 30) for 36 hours under a positive pressure of argon gas forming a dark brown solution and a white salt precipitate. The Absolute Ethanol was then distilled off and the remaining sticky, brown product was left to dry overnight under argon. The dried product was then washed with 400mL of Ethyl Acetate (EtOAc) and 100mL of 1M NaOH. Using a 1000mL seperatory funnel, the bottom layer was removed. The top (EtOAc) layer was then washed with 100mL of 1M NaOH, 100mL of distilled water, and 100mL of saturated brine solution. The remaining golden solution was dried with several scoops of anhydrous Sodium Sulfate and the excess EtOAc solvent was boiled off using a rotary evaporator. The product was left overnight to recrystallize in approximately 100mL of the remaining EtOAc solvent. The crystallized product was then removed using vacuum filtration on a Buchner funnel. Yields from this experiment ranged from 25-30% in most cases with a melting range from 77-83°C. Proton and carbon-13 NMR were taken of the recrystallized product. **(See Appendix A)**

NMR data:

H NMR($CDCl_3$): δ 3.402-3.931 (4H,m), 4.049-4.087 (6H,m), 6.874-7.002 (4H,m).

^{13}C NMR ($CDCl_3$): δ 61.169, 71.607, 114.179, 122.237, 148.955

Synthesis of 1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene (3)

1,2-*bis*[2-hydroxyethoxy]benzene(2) (1.995g, 10mmol) was dried under argon for 4 hours, while maintaining a temperature between 70-80˚C. 4-5 drops of Tin(IV) Chloride were then added to the flask. After the Tin(IV) Chloride was added, Epichlorohydrin (2.5mL, 32mmol) was added drop wise to the reaction mix. As the solid dissolved and stirred, the solution was allowed to react under argon for 2 hours. The reaction was monitored using TLC. The Tin(IV) Chloride catalyst was then deactivated using 15mL of distilled water and the new 1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene(3) product was dissolved in 70mL of Ethyl Ether and washed three times with 20mL of 8% $NaHCO_3$, 20mL of distilled water, and 20mL of saturated brine solution, and then separated using a small seperatory funnel. The remaining Ethyl Ether layer was dried using several scoops of anhydrous Sodium Sulfate. The dried solution was then decanted and rotary evaporated to remove the Ethyl Ether and excess Epichlorohydrin. The remaining product was a golden syrupy compound that massed 3.221g (8.4mmol). Yields from this experiment were approximately 83.5% in most cases. Proton and carbon-13 NMR were taken of the product. **(See Appendix A)**

NMR data:

H NMR($CDCl_3$): δ 3.156-3.236 (1.6 H,m), 3.526-3.776 (11.15 H,m), 3.777- 3.895 (4.2 H,m), 3.922-4.005 (2.4 H,m), 4.082-4.102 (3.8 H,m), 6.786-6.891 (4 H,m).

^{13}C NMR ($CDCl_3$): δ 45.607, 67.951, 70.108, 70.330, 72.532, 113.642, 121.713

Scheme 1

Synthesis of 1,2-bis[2-(2,3-epoxypropoxy)ethoxy]benzene (4)[1]

1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene(3) (7.66g, 20mmol) was added to a 250mL round-bottom flask. Absolute Ethanol (100ml) was added to the flask and stirred in an ice bath for 10 minutes or until all of the 1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene(3) had dissolved. To protect the reaction from absorbing water, KOH (2.60g, 40mmol) was added to the round bottom flask. After 2-3 hours, the reaction mix was transferred to a 200mL flask. 30mL of distilled water was then added and the solution was monitored using pH paper. The reaction mix was neutralized using 1% HCL until pH reached approximately 6-7. The reaction mixture was then transferred to a seperatory funnel and 1,2-bis[2-(2,3-epoxypropoxy)ethoxy]benzene (4) was extracted with 100ml of Ethyl Ether. The product was washed three times with 20mL of distilled water, once with 20mL of brine solution, and then dried using several scoops of anhydrous Sodium Sulfate. Crude product was transferred into a 250ml round bottom flask and solvent evaporated under high vacuum without heat. 6.27g (19mmol) of crude product was recovered producing a yield of 95%[1]. Carbon-13 and proton NMR were taken of our product. (**See Ammozgar, 2006-2007**)

NMR data:

H NMR($CDCl_3$): δ 2.562-2.567 (1.75 H,m), 2.705-2.717 (1.75 H,m), 3.03-3.108

(1.7 H,m), 3.419-3.463 (2.2 H,m), 3.556-3.747 (4 H,m), 3.7856-3.821 (5.8 H,m), 4.085-4.18 (4 H,m), 6.850-6.874 (4 H,m).

^{13}C NMR ($CDCl_3$): δ 44.293, 50.930, 68.999, 70.017, 71.469, 115.057, 122.107, 149.070

Scheme 3 (THP protection)

Synthesis of Protected 1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene (5)

1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene(3) (3.735g, 9.75mmol) was stirred in a round-bottom flask at 0°C in 90mL of Dichloromethane. Dihydropyran (7.2mL, 79mmol), and TsOH (0.017g, 0.089mmol) were then added to the reaction flask and allowed to stir. After 10 minutes, the ice bath was removed from the flask and the solution was allowed to react at room temperature overnight. The solution was then washed with equal parts of Ethyl Ether and a solution made from 40ml brine solution, 40ml saturated Sodium Bicarbonate solution, and 80ml of distilled water. The organic layer was saved and washed twice with 40mL of brine solution. The solution was then dried with several scoops of anhydrous Sodium Sulfate in 100mL of Toluene. Finally, the solution was rotary evaporated to remove excess solvent. The final product massed 6.221g, which produced a yield of 116%. Carbon-13 and proton NMR were taken. (**See Appendix A**)

NMR data:

H NMR($CDCl_3$): δ 1.19-1.74 (15.4 H,m), 3.68-4.15 (29 H,m), 3.7856-3.821 (5.8 H,m), 4.78-4.95 (2 H,m), 6.88-6.90 (4 H,m).

^{13}C NMR ($CDCl_3$): δ 19.486, 25.55, 30.86, 44.83, 62.759, 70.28, 71.40, 75.27, 75.59, 76.85, 98.81, 115.13, 121.78, 129.12, 149.13

Preparation of the Cesium Salt (6)

In a three-neck round-bottom flask, 1,2-bis[2-hydroxyethoxy]benzene(2) (1.845g, 9.3mmol) was added to Cesium Hydroxide monohydrate (3.136g, 18.6mmol) in approximately 100mL of Toluene. The solution was boiled on the rotary evaporator until most of the Toluene had been removed. The remaining solvent and water was removed using a vacuum pump. A white solid remained as our cesium salt compound (6).

Synthesis of the Protected Dihydroxydibenzo-26-Crown-8 (1)

The protected 1,2-bis[2-(3-chloro-2-hydroxypropoxy)ethoxy]benzene(5) (5.106g, 9.3mmol) was dissolved in low water THF and added to the same three-neck round-bottom flask containing the cesium salt compound (6). The solution was then heated to reflux and left under argon gas for three days. The THF solvent was then boiled off using the rotary evaporator. The remaining brown, syrupy compound was washed with 50mL of distilled water and 50mL of Dichloromethane. The Dichloromethane layer was then separated and saved, while the water layer was washed three times more with 50mL of

Dichloromethane to extract any remaining product still in solution. The combined Dichloromethane layers were then dried twice with several scoops of anhydrous Sodium Sulfate. After drying, all solvent was removed using the rotary evaporator and vacuum pump. Proton and carbon-13 NMR were taken. **(See Appendix A)**

NMR data:

H NMR($CDCl_3$): δ 1.53-1.70 (12 H,m), 3.71-4.16 (26 H,m), 4.79 (2 H,m)

6.91-6.97 (4 H,m).

^{13}C NMR ($CDCl_3$): δ 19.48, 25.43, 30.67, 44.79, 62.68, 68.77, 70.28, 71.99, 98.83,

115.92, 122.54, 149.15

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Appendix A (^{1}H and ^{13}C NMR)

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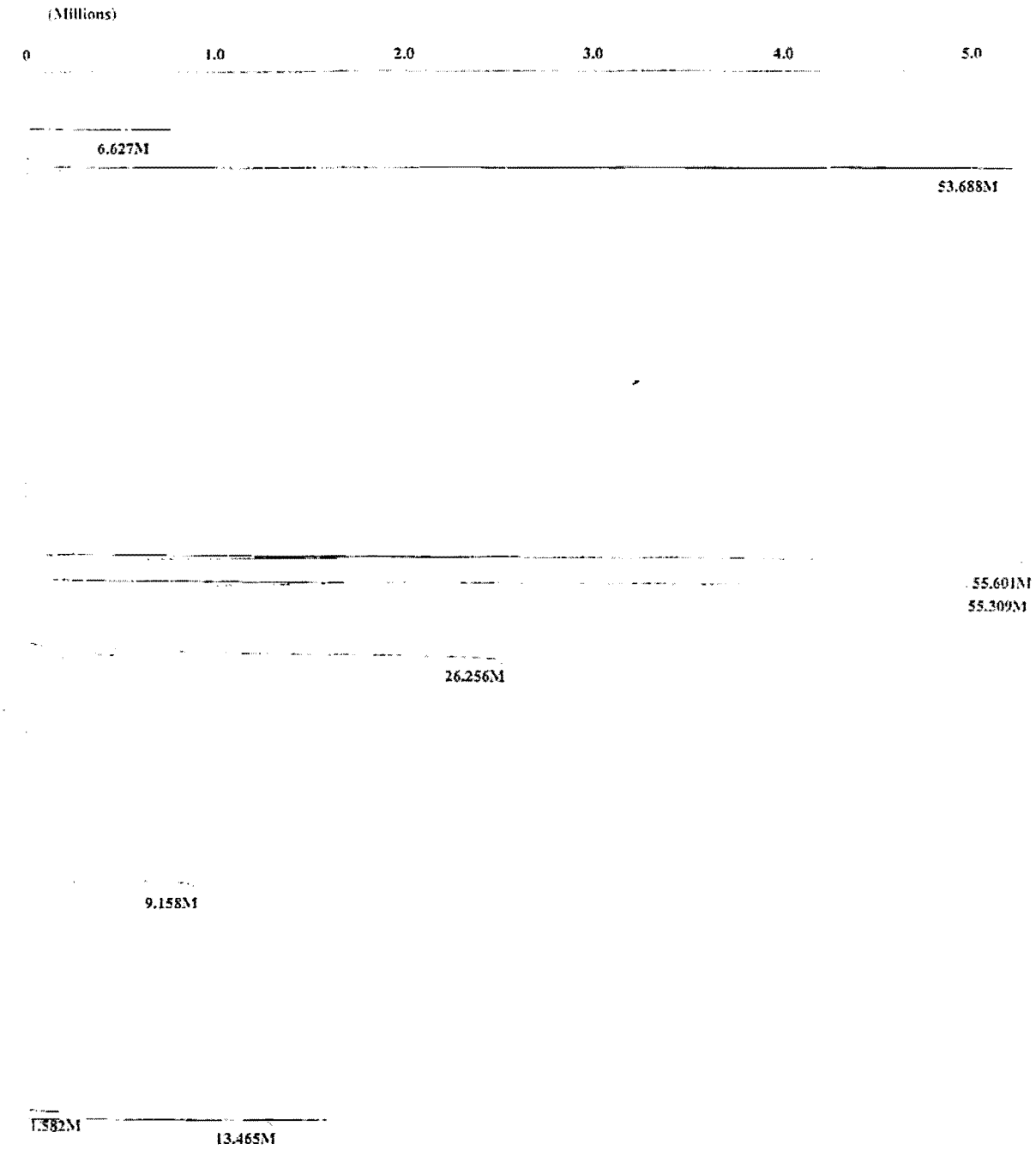

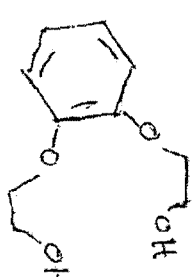

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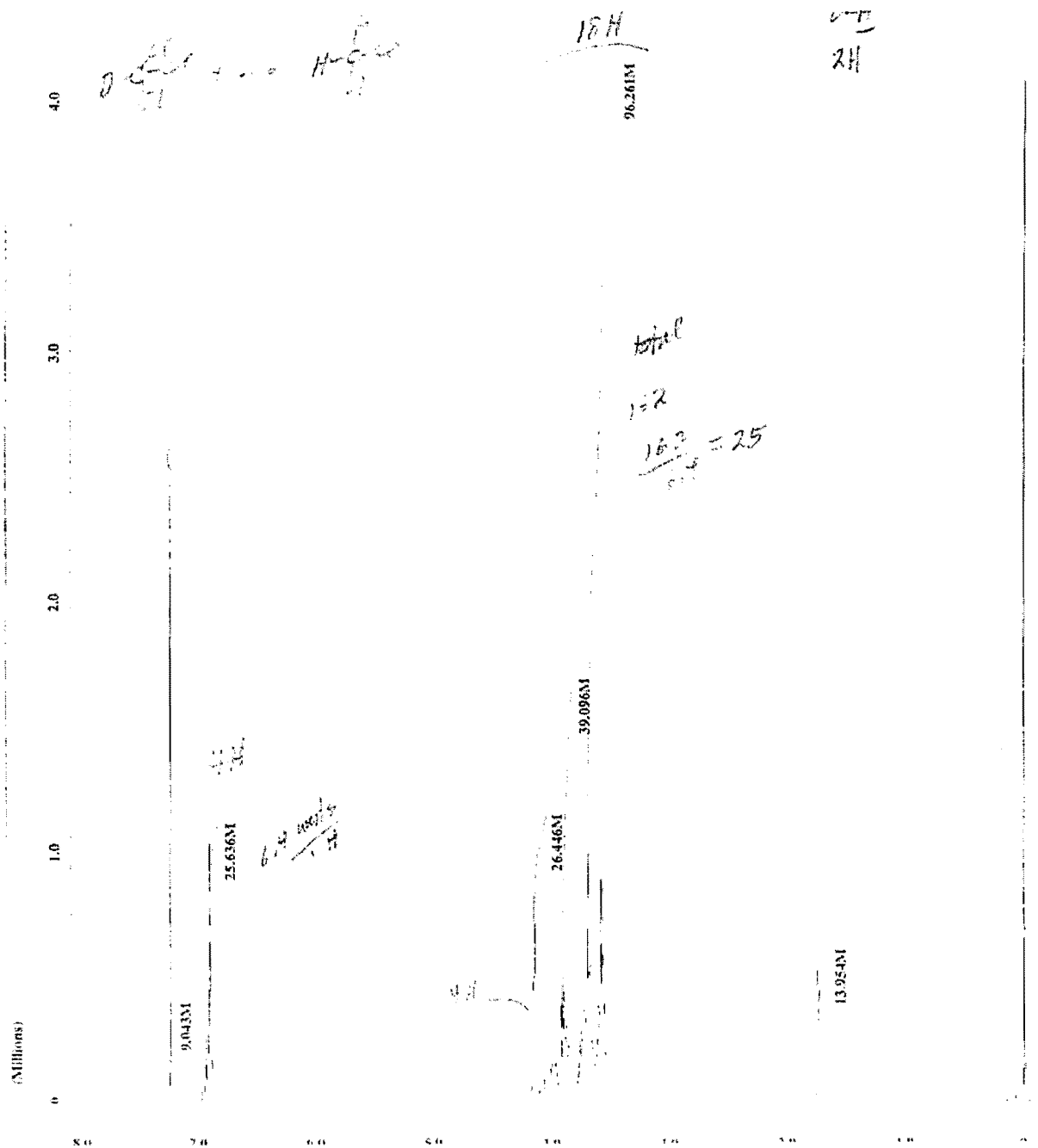

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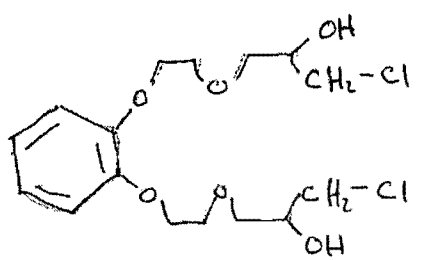

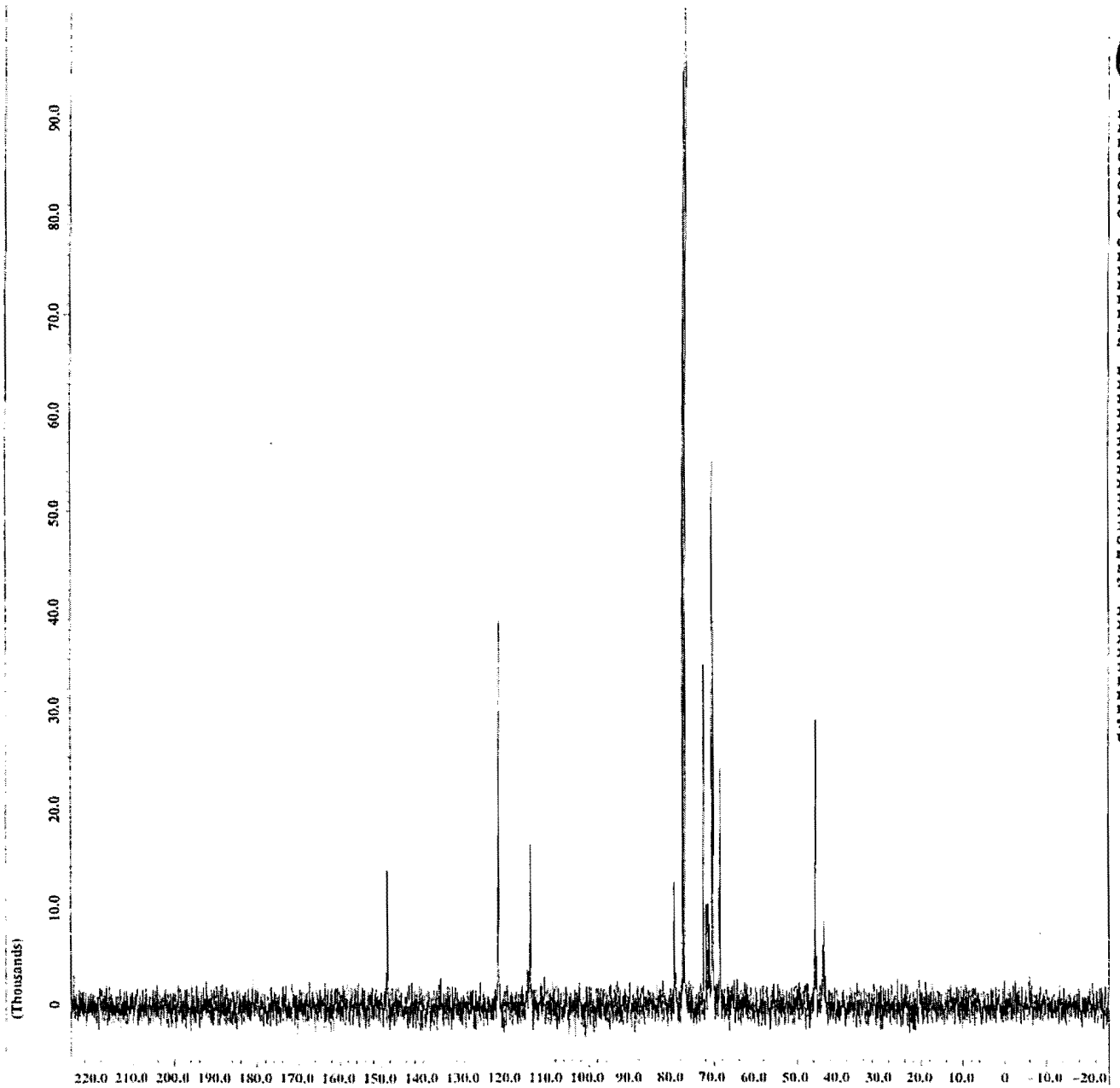

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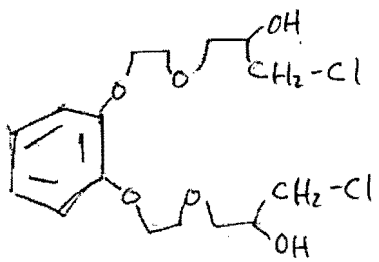

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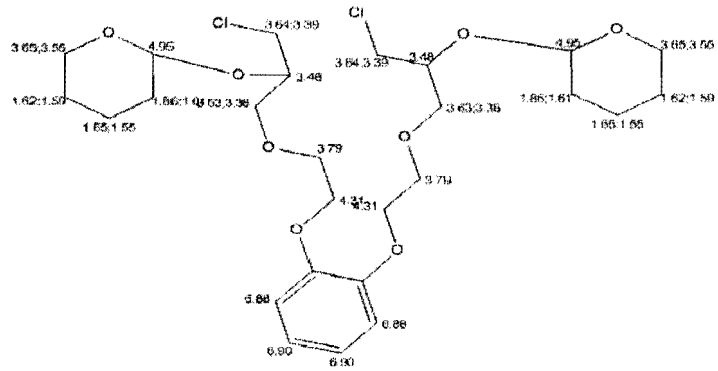

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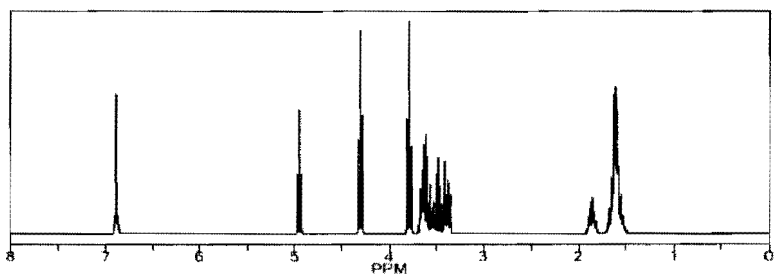

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CH 4.95		3.62	tetrahydropyran
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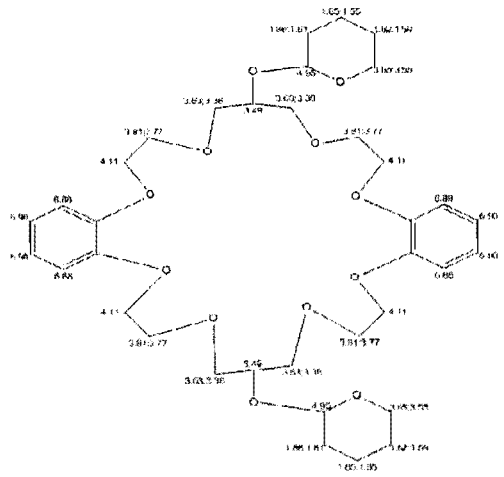
ChemNMR ^{1}H Estimation



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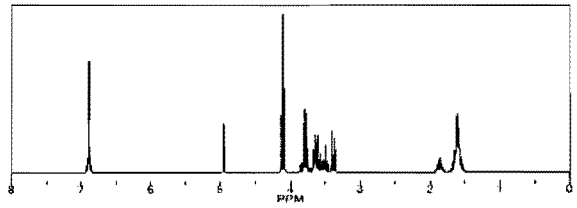

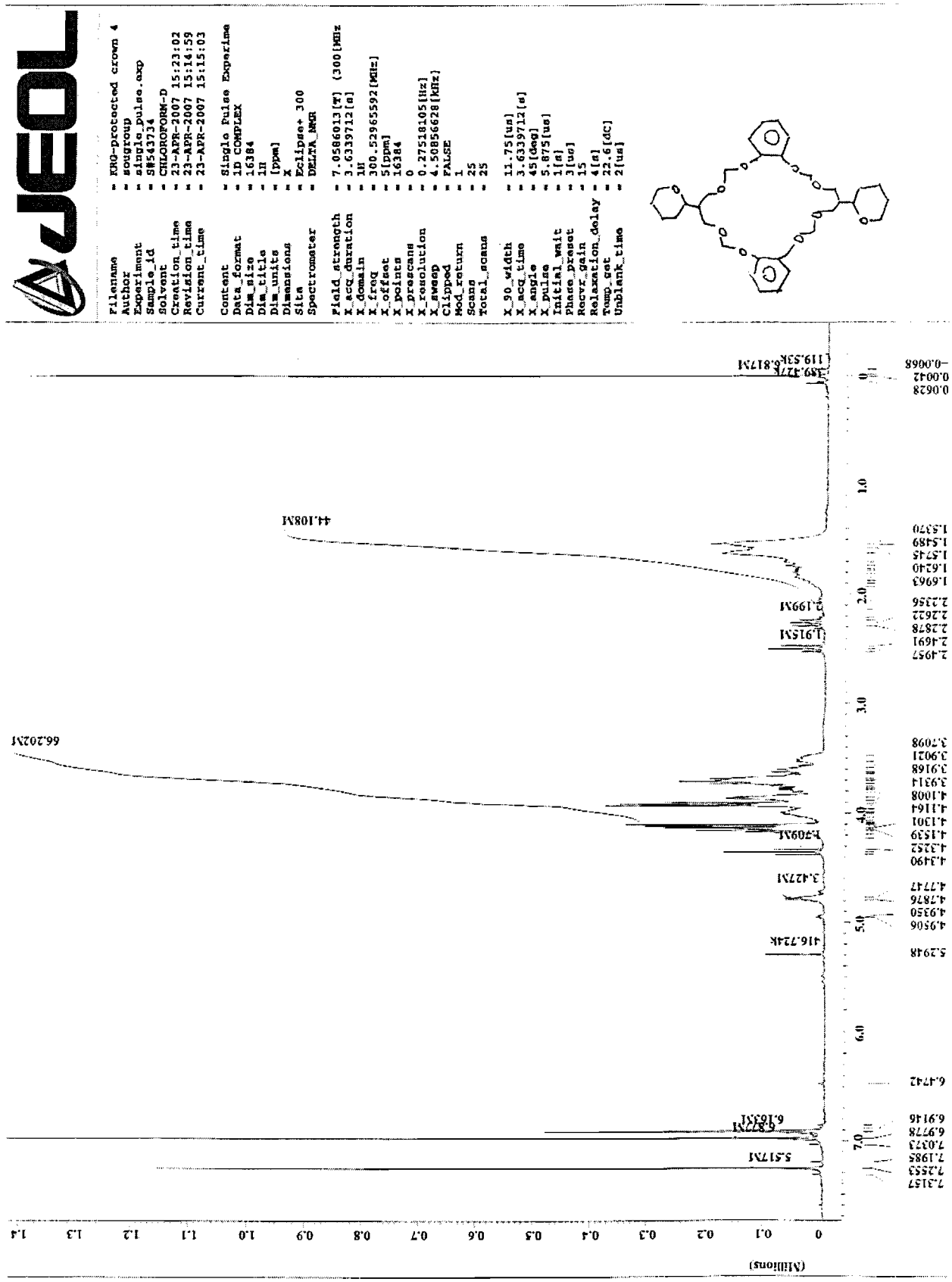
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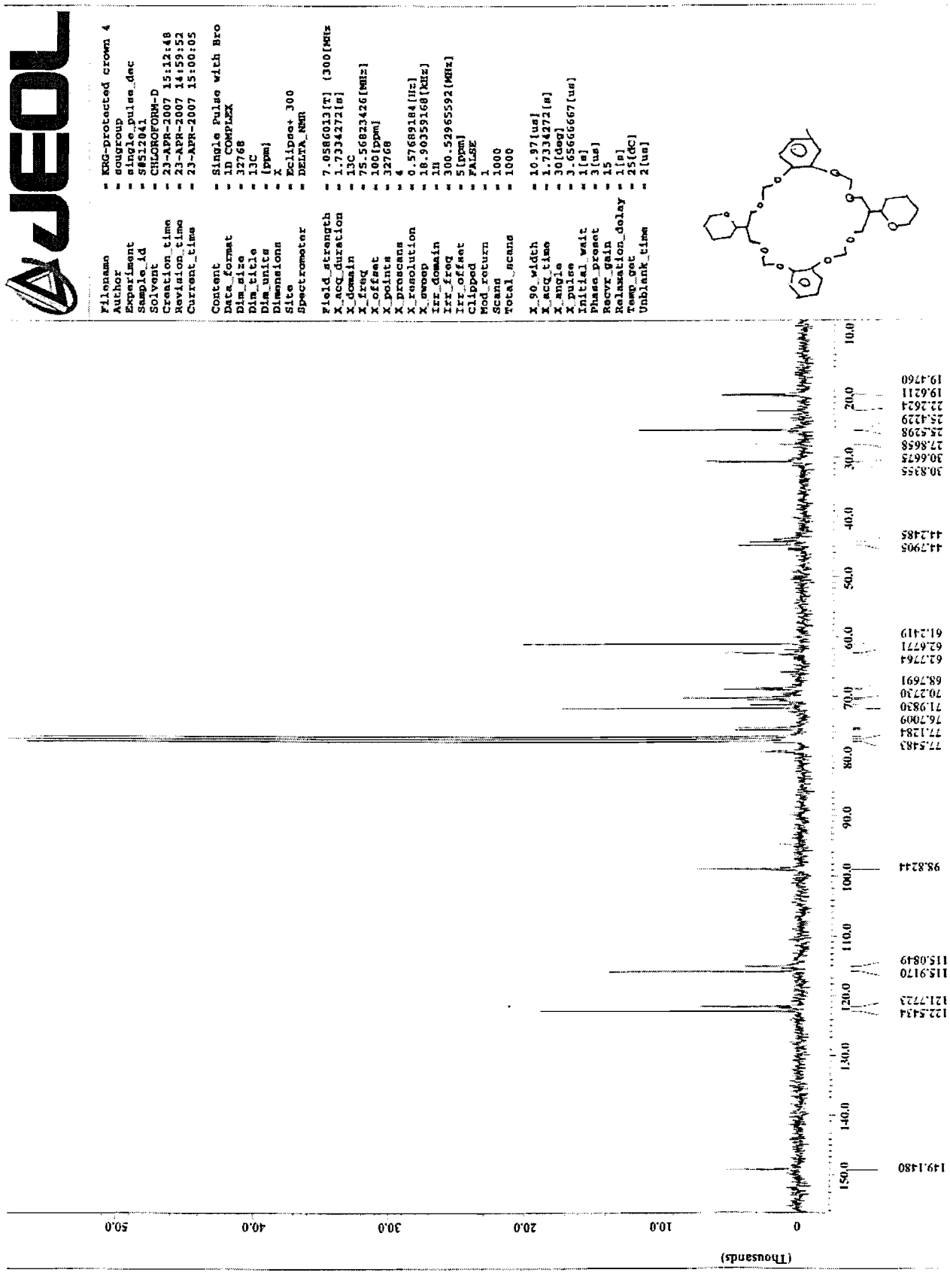
X_acq_time = 3.633971 2[s]
X_angle = 45[deg]
X_pulse = 5.875[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 4[s]
Temp_get = 22.6[dC]
Unblank_time = 2[us]
(Millions)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
7.3157
7.2553
7.1985
7.0373
6.9778
6.9146
6.4742
5.2948
4.9506
4.9350
4.7876
4.7747
4.3490
4.3252
4.1539
4.1301
4.1164
4.1008
3.9314
3.9168
3.9021
3.7098
2.4957
2.4691
2.2878
2.2622
2.2356
1.6963
1.6240
1.5745
1.5489
1.5370
0.0628
0.0042
-0.0068
119.53K
89.327K
8.817M
44.108M
2.199M
1.915M
66.202M
5.709M
3.427M
416.724K
6.827M
6.163M
5.517M
1.0
2.0
3.0
4.0
5.0
6.0
7.0


JEOL
Filename = KRG-protected crown 4
Author = dougroup
Experiment = single_pulse_dec
Sample_id = S#512041
Solvent = CHLOROFORM-D
Creation_time = 23-APR-2007 15:12:48
Revision_time = 23-APR-2007 14:59:52
Current_time = 23-APR-2007 15:00:05
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 300
Spectrometer = DELTA_NMR
Field_strength = 7.05860131[T] (300[MHz
X_acq_duration = 1.73334272[s]
X_domain = 13C
X_freq = 75.568223426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.57689184[Hz]
X_sweep = 18.90359168[KHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 1000
Total_scans = 1000
X_90_width = 10.97[us]
X_acq_time = 1.73334272[s]
X_angle = 30[deg]
X_pulse = 3.65666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 25[dC]
Unblank_time = 2[us]
149.1480
122.5434
121.7723
115.9170
115.0849
98.8244
77.5483
77.1284
76.7009
71.9830
70.2730
68.7691
63.7764
62.6771
61.2419
44.7905
44.2485
30.8355
30.6675
27.8658
25.4298
25.4229
22.2624
19.6211
19.4760
(Thousands)
0
10.0
20.0
30.0
40.0
50.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0